

**WATER-BASED 2K COATING COMPOSITIONS**

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**Abstract**

Disclosed is a non-foaming, water-based coating composition made by blending a water-based, hydroxy functional, acrylic polymeric component with a water dispersible isocyanate component. The water-based, hydroxy functional, acrylic polymeric component includes a vinyl-type polymer product having hydrolyzable silyl groups incorporated onto its backbone. The water dispersible isocyanate component includes a polyisocyanate which is based on hexamethylene diisocyanate.

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<b>(21) International Application Number:</b> PCT/US99/09729 <b>(22) International Filing Date:</b> 4 May 1999 (04.05.99) <b>(30) Priority Data:</b> 60/085,081 12 May 1998 (12.05.98) US <b>(71) Applicant:</b> PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US). <b>(72) Inventors:</b> NATESH, Anbazhagan; 120 Kent Drive, North Wales, PA 19454-1925 (US). HAYES, Deborah, E.; 7055 Shannon Road, Verona, PA 15147 (US). HARLEY, Mark, A.; 530 Sixth Street, Oakmont, PA 15139 (US). BURKHOLDER, Mary, Jo; 605 Green Hill Court, Mars, PA 16046 (US). <b>(74) Agents:</b> CHIRGOTT, Paul, S.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> WATER-BASED 2K COATING COMPOSITIONS  <b>(57) Abstract</b>  Disclosed is a non-foaming, water-based coating composition made by blending a water-based, hydroxy functional, acrylic polymeric component with a water dispersible isocyanate component. The water-based, hydroxy functional, acrylic polymeric component includes a vinyl-type polymer product having hydrolyzable silyl groups incorporated onto its backbone. The water dispersible isocyanate component includes a polyisocyanate which is based on hexamethylene diisocyanate.		

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# **WATER-BASED 2K COATING COMPOSITIONS**

## **FIELD OF THE INVENTION**

The present invention is directed to a non-foaming, water-based  
5 coating composition made by blending a water-based, hydroxy functional, acrylic  
polymeric component with a water dispersible isocyanate component.

## **BACKGROUND OF THE INVENTION**

There is a continuing need, particularly in the coating industry, to  
10 provide compositions which contain little, if any, volatile organic components.  
Additionally, it would be desirable to provide such compositions which do not  
depend on organic isocyanates for curing.

However, approaches to meet these challenges generally have  
involved disadvantageous compromises among desirable coating composition  
15 properties such as storage stability of the coating composition; and desirable  
properties of the cured film such as weatherability. For example, it is known that  
coatings made by blending organic-based, acrylic polymers with organic isocyanates  
produces coatings which, when cured, are weather resistant. However, when  
attempting to convert such an organic-based system to a water-based system  
20 problems such as storage stability are encountered.

Specifically, it is known that, when blending conventional water-  
based, acrylic polymers with conventional water dispersible isocyanates, carbon  
dioxide is often a by-product. This by-product, in turn, causes the coating to foam  
such that its volume can increase by over 100% over a relatively short period of  
25 time. This foam generation can also have an adverse effect on the cured film if  
special precautions are not taken during the application and/or curing processes.  
Accordingly, due to these and other deficiencies, water-based coatings of this type  
are virtually unusable for most commercial applications.

Objects of the present invention are to help meet these challenges. Other objects of the invention will become apparent to those skilled in the art after reading the following specification.

## 5 SUMMARY OF THE INVENTION

The present invention provides a non-foaming, water-based coating composition made by reacting a water-based, hydroxy functional, acrylic polymeric component with a water dispersible isocyanate component. The water-based, hydroxy functional, acrylic polymeric component includes a vinyl-type polymer product having hydrolyzable silyl groups incorporated onto its backbone. The water  
10 dispersible isocyanate component includes a polyisocyanates which is based on hexamethylene diisocyanate.

As used herein, the term "non-foaming" means that the volume change, due to the generation of a gaseous by-product, of a coating stored in a  
15 closed container at temperatures of up to about 50°C. for time periods of up to 24 hours, does not exceed 5 percent; and preferably, the volume change of a coating when subjected to these conditions does not exceed 1 percent.

## DETAILED DESCRIPTION OF THE INVENTION

20 Non-foaming, water-based coating compositions made in accordance with this invention include, among other things, a water-based, hydroxy functional, acrylic polymeric component, and a water dispersible isocyanate component.

The water-based, hydroxy functional, acrylic polymeric component includes a vinyl-type polymer product having hydrolyzable silyl groups incorporated  
25 onto its backbone. The vinyl-type polymer has acid functionality sufficient to provide an acid value ranging from 5 to 160; preferably from 10 to 120. The aforesaid acid functionality allows the vinyl-type polymer to be solubilized or

dispersed in water upon at least partial neutralization of acid groups with an appropriate base.

The vinyl-type polymer also has sufficient hydrolyzable silyl groups to provide a silicon content ranging from 0.40 to 6.0 percent; preferably from 0.50 to 3.0 percent. These percentages are by weight based upon the total weight of the vinyl-type polymer. Typically, the silicon atoms of the hydrolyzable silyl groups on the vinyl-type polymer are separated by at least two atoms from the backbone of the polymer.

Moreover, the vinyl-type polymer used when practicing this invention typically has a hydroxyl value which does not exceed 10. While the molecular weight of the vinyl-type polymers may vary, the solution polymerized vinyl-type polymer, prior to dispersion (or solubilization) in water, typically has a number average molecular weight which does not exceed 12,000; and preferably, a number average molecular weight which does not exceed 10,000. These molecular weights are determined by gel permeation chromatography utilizing a polystyrene standard.

The choice of solution-polymerized, vinyl-type polymer which can be used when practicing this invention is not particularly limited provided that it contains the aforesaid acid functionality and hydrolyzable silyl groups. Examples of suitable vinyl-type polymers which can be employed are described *infra* wherein the solution-polymerized vinyl-type polymer is prepared from the addition copolymerization of components comprising: an ethylenically unsaturated silane monomer containing at least one hydrolyzable silyl group, an ethylenically unsaturated acid and/or anhydride thereof, and at least one other copolymerizable vinyl-type monomer.

Examples of ethylenically unsaturated silane monomers which can be employed in the preparation of suitable vinyl-type polymers include: ethylenically unsaturated alkoxy silanes and ethylenically unsaturated acyloxy silanes. Specific examples of the foregoing include: acrylatoalkoxysilanes, such as gamma-acryloxypropyl trimethoxysilane and gamma-acryloxypropyl triethoxysilane; methacrylatoalkoxysilanes, such as gamma-methacryloxypropyl trimethoxysilane,

gamma-methacryloxypropyl triethoxysilane and gamma-methacryloxypropyl tris-(2-methoxyethoxy) silane; acyloxysilanes including, for example, acrylato acetoxysilanes, methacrylato acetoxysilanes and ethylenically unsaturated acetoxysilanes such as acrylatopropyl triacetoxysilane and methacrylatopropyl triacetoxysilane. Of the aforesaid ethylenically unsaturated silane monomers, it is preferred to utilize monomers which upon vinyl addition copolymerization will result in vinyl-type polymer products in which the silicone atoms of the hydrolyzable silyl groups on the vinyl-type polymer are separated by at least two atoms from the backbone of the polymer.

Examples of ethylenically unsaturated acids and/or anhydrides thereof which can be employed in the preparation of suitable vinyl-type polymers include: acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, maleic anhydride, citraconic anhydride, itaconic anhydride, ethylenically unsaturated sulfonic acids and/or anhydrides such as sulfoethyl methacrylate, and half esters of maleic and fumaric acids, such as butyl hydrogen maleate and ethyl hydrogen fumarate in which one carboxyl group is esterified with an alcohol. Ethylenically unsaturated carboxylic acids and/or anhydrides thereof are preferred.

Examples of other copolymerizable vinyl-type monomers which can be employed in the preparation of suitable vinyl-type polymers include: the alkyl acrylates, such as methyl acrylate, ethyl acrylate, butyl acrylate, propyl acrylate, 2-ethylhexyl acrylate and isobornyl acrylate; the alkyl methacrylates, such as methyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, lauryl methacrylate and isobornyl methacrylate; hydroxyalkyl acrylates and methacrylates such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethylmethacrylate and hydroxypropyl methacrylate; N-alkoxymethyl acrylamides and methacrylamides such as N-butoxymethyl acrylamide, N-butoxymethyl methacrylamide, N-ethoxymethyl acrylamide and N-ethoxymethyl methacrylamide; epoxy functional ethylenically unsaturated monomers such as glycidyl methacrylate and glycidyl acrylate; and unsaturated nitriles, such as acrylonitrile, methacrylonitrile and ethacrylonitrile. Other ethylenically unsaturated

monomers (vinyl monomers) which can be used in addition to the aforesaid vinyl-type monomers include: vinyl aromatic hydrocarbons (optionally substituted, for example, by halo atoms) such as styrene, alpha-methyl styrene, alpha-chloromethyl styrene and vinyl toluene; and vinyl aliphatic hydrocarbons (optionally substituted, for example, by halo atoms) such as vinyl acetate and vinyl chloride.

Although the components for preparing the vinyl-type polymer where desired may include hydroxyl-functional, ethylenically unsaturated monomers such as the hydroxyalkyl acrylates and methacrylates described above, they can be prepared without utilization of such hydroxyl-functional monomers for the vinyl-type polymer, and typically, suitable vinyl-type polymers can be prepared from components essentially or completely free of such hydroxyl-functional, ethylenically unsaturated monomers. For example, the vinyl-type polymer typically has a hydroxyl value of less than or equal to 10.

When the solution-polymerized, vinyl-type polymer is prepared from the addition copolymerization of components as described above, typically from 5 to 13 percent by weight of the ethylenically unsaturated acid and/or acid anhydride thereof and from 12 to 87 percent by weight of the other copolymerizable vinyl-type monomer are employed (the percentages being based on the total weight of copolymerizable monomers used in the preparation of the vinyl-type polymer). The amount of the ethylenically unsaturated silane monomer typically is chosen to provide a silicon content of the vinyl-type polymer in the range of from 0.40 to 6.0, preferably from 0.50 to 3.0, percent by weight based on the total weight of the vinyl-type polymer.

Typically, the vinyl-type polymer is formed by solution interpolymersing the ethylenically unsaturated monomers in the presence of a vinyl polymerization initiator, examples of which include: azo compounds such as alpha-alpha'-azobis(isobutyronitrile), 2,2'-azobis (methylbutyronitrile) and 2,2'-azobis(2,4-dimethylvaleronitrile); peroxides such as benzoyl peroxide, cumene hydroperoxide and t-amylperoxy-2-ethylhexanoate; tertiary butyl peracetate; tertiary butyl perbenzoate; isopropyl percarbonate; butyl isopropyl peroxy



carbonate; and similar compounds. The quantity of initiator employed can be varied considerably. However, in most instances, it is desirable to utilize from about 0.1 to about 10 percent by weight of initiator based on the total weight of copolymerizable monomers employed.

5           A chain modifying agent or chain transfer agent may be added to the polymerization mixture. The mercaptans, such as dodecyl mercaptan, tertiary dodecyl mercaptan, octyl mercaptan, hexyl mercaptan and the mercaptoalkyl trialkoxysilanes such as 3-mercaptopropyl trimethoxysilane may be used for this purpose as well as other chain transfer agents such as cyclopentadiene, allyl acetate,  
10 allyl carbamate, and mercaptoethanol.

          The polymerization reaction for the mixture of monomers to prepare the vinyl-type polymer can be carried out in an organic solvent medium utilizing conventional solution polymerization procedures which are well known in the addition polymer art as illustrated with particularity in, for example, U.S. Pat. Nos.  
15 2,978,437; 3,079,434 and 3,307,963. Organic solvents which may be utilized in the polymerization of the monomers include virtually any of the organic solvents heretofore employed in preparing acrylic or vinyl polymers such as, for example, alcohols, ketones, aromatic hydrocarbons or mixtures thereof. Illustrative of organic solvents of the above type which may be employed are alcohols such as lower  
20 alkanols containing 2 to 4 carbon atoms including ethanol, propanol, isopropanol, and butanol; ether alcohols such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, propylene glycol monomethyl ether, and dipropylene glycol monoethyl ether; ketones such as methyl ethyl ketone, methyl N-butyl ketone, and methyl isobutyl ketone; esters such as butyl acetate; and aromatic hydrocarbons such  
25 as xylene, toluene, and naphtha.

          As mentioned previously, the choice of suitable solution-polymerized, vinyl-type polymers which can be employed is not particularly limited provided that it contains the aforesaid acid functionality, hydrolyzable silyl groups and stability in aqueous medium as described above. For example, another way of preparing  
30 suitable solution-polymerized, vinyl-type polymers is by vinyl addition

copolymerizing components comprising an ethylenically unsaturated anhydride and at least one other copolymerizable vinyl-type monomer wherein amino functionality of an amino-functional compound containing at least one hydrolyzable silyl group has been reacted with an anhydride group of the vinyl-type polymer. More  
5 specifically, an ethylenically unsaturated anhydride and at least one other copolymerizable vinyl-type monomer (which does not contain a hydrolyzable silyl group) can be vinyl addition polymerized in an organic solvent as described above utilizing a vinyl polymerization initiator as described above to form an intermediate vinyl polymer product. Thereafter, anhydride functionality from the resulting  
10 intermediate product is reacted with amino functionality from an amino-functional compound containing hydrolyzable silyl groups to produce the vinyl-type polymer product for preparation of an aqueous solution or dispersion of the invention.

Examples of amino-functional compounds containing hydrolyzable silyl groups which may be utilized in the reaction with anhydride functionality from  
15 the aforesaid intermediate vinyl polymer product include: gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, beta-aminoethyl triethoxysilane, gamma-aminopropylmethyl diethoxysilane, gamma-aminopropylethyl diethoxysilane, gamma-aminopropylphenyl diethoxysilane, delta-aminobutyl triethoxysilane, delta-aminobutylethyl diethoxysilane and  $(\text{CH}_3\text{O})_3\text{Si}-$   
20  $(\text{CH}_2)_3\text{-NH-(CH}_2)_3\text{-Si(OCH}_3)_3$ .

Dispersion or solubilization of the vinyl-type polymer in water is typically carried out via at least partial neutralization of acid functionality of the polymer with a base such as ammonia, an amine or a mixture thereof. Examples of amines which may be utilized include: aliphatic amines such as monoethylamine,  
25 diethylamine and triethylamine; alkanolamines such as dimethylethanol amine, monoethanol amine, diethanol amine and triethanol amine; and cyclic amines such as pyridine and piperidine. In many cases ammonia is preferred for low temperature curing.

The water dispersible isocyanate component includes a polyisocyanate  
30 which is based on hexamethylene. Typically, such a polyisocyanate used when

practicing this invention has an average NCO functionality ranging from 2 to 6. Moreover, these polyisocyanates contain the following:

- a) a polyisocyanate adduct prepared from 1,6-hexamethylene diisocyanate or a mixture of hexamethylene diisocyanate with up to 70% by weight, based on the weight of the diisocyanates, of another diisocyanate, and
- b) at least 10 percent by weight, based on the weight of the polyisocyanate adduct, of an emulsifier which is based on the reaction product of:
  - i) a monohydroxy functional polyether wherein the ethylene oxide portion of the polyether has a molecular weight ranging from 200 to 1000 and the polyether has a total molecular weight ranging from 200 to 1500, and
  - ii) either a polyisocyanate adduct which corresponds to component a), above, or another polyisocyanate.

The polyisocyanate compositions used when practicing this invention have an average functionality of at least 2, preferably of at least 2.5. The upper limit for the functionality is 6, preferably 4.5.

Suitable polyisocyanate adducts include those containing isocyanurate, uretdione, biuret, urethane, allophanate, carbodiimide or oxadiazinetriene groups. Processes for the preparation of polyisocyanate adducts containing these groups are known and described in U.S. Pat. Nos. 4,518,522 and 4,663,377. Preferred polyisocyanate adducts are those containing isocyanurate groups, mixtures of isocyanurate groups and allophanate groups and mixtures of isocyanurate groups and uretdione groups.

The polyisocyanate adducts are prepared from 1,6-hexamethylene diisocyanate. However, it is also possible to prepare the polyisocyanate adducts from 1,6-hexamethylene diisocyanate in admixture with up to 70 percent, preferably up to 50 percent, based on the total weight of diisocyanates, of an additional diisocyanate, preferably a diisocyanate containing (cyclo)aliphatically bound

isocyanate groups. Suitable diisocyanates of this type have been disclosed in the above-mentioned references. Preferred diisocyanates include: 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (isophorone diisocyanate or IPDI) and bis-(4-isocyanatocyclohexyl)-methane.

5                   Suitable emulsifiers include the reaction products of polyisocyanates with monohydroxy functional polyethers. Examples of suitable polyisocyanates include: the polyisocyanate adducts previously set forth and, in addition, other polyisocyanates, preferably polyisocyanates containing (cyclo)aliphatically bound isocyanate groups. These other polyisocyanates include polyisocyanate adducts  
10 prepared from diisocyanates other than 1,6-hexamethylene and also monomeric polyisocyanates. These other polyisocyanate adducts and monomeric polyisocyanates have been described in the references.

Suitable monohydroxy functional polyethers are those wherein the ethylene oxide portion has a minimum molecular weight of 200, preferably 250 and  
15 more preferably 300. The upper limit for the molecular weight of the ethylene oxide portion is 1000, preferably 950; more preferably 900; and even more preferably 800. The minimum molecular weight for the entire polyether is 200; preferably 250; and more preferably 300. The upper limit for the molecular weight of the polyether is 1500; preferably 1200; more preferably 1000; and even more  
20 preferably the molecular weight is the same as the maximum molecular weight of the ethylene oxide portion. In other words, a preferred family of polyethers are based exclusively on ethylene oxide.

The polyethers are prepared by reacting starter molecules with ethylene oxide or optionally with a mixture of ethylene oxide and another alkylene  
25 oxide, preferably propylene oxide or butylene oxide and more preferably propylene oxide. The presence of these other alkylene oxides does not increase the hydrophilicity of the polyethers and, therefore, their use is not preferred. However, polyethers based exclusively on ethylene oxide and having ethylene oxide molecular weights at the upper end of the previously discussed ranges may be crystalline.  
30 Small amounts of the other alkylene oxides may be incorporated into these

polyethers in order to reduce their tendency to crystallize. However, it is more preferred to reduce the tendency to crystallize by reducing the molecular weight of the polyether.

Suitable starter molecules for the production of the monofunctional  
5 polyethers include monoalcohols containing 1 to 12 carbon atoms, preferably 1 to 4 carbon atoms, such as methanol, ethanol, propanol or butanol, cyclohexanol, 3-methyl-3-hydroxymethyl-oxetane and phenol. Additional cyclic starter molecules are set forth in U.S. Pat. No. 4,472,550.

The production of the emulsifiers takes place by reacting the aliphatic  
10 polyisocyanates with the monohydroxy functional polyethers at a molar ratio of at least 1:1, preferably in the range from 2:1 to 1000:1. The emulsifiers can either be produced in a separate step and then mixed with polyisocyanate a) to form the composition of the present invention, or they can be produced in situ. In this latter method the polyisocyanate is mixed with a quantity of the monohydroxy functional  
15 polyether such that the composition is produced in situ. If the emulsifiers are produced in a separate step, the starting materials are reacted at an NCO/OH equivalent ratio ranging from 2:1 to 6:1. If, however, the emulsifiers are produced in situ, a higher excess of isocyanate groups within the above-mentioned range can be used.

20 The quantity of the emulsifier which is mixed with the polyisocyanate or the quantity of monohydroxy functional polyether which is added to the polyisocyanate to prepare the polyisocyanate compositions in situ is calculated such that the polyisocyanate compositions contain a lower limit of at least 10 percent by weight, preferably at least 12 percent by weight of ethylene oxide units arranged in  
25 polyether chains. The upper limit is not critical, but is preferably 20 percent by weight, more preferably 15 percent by weight, of ethylene oxide units arranged in polyether chains.

In order to reduce the viscosity of the polyisocyanate preparations, small quantities (*i.e.*, about 1 to 10 percent by weight, based on the solvent-free  
30 polyisocyanate composition), of an organic solvent such as ethylacetate, acetone or

methylketone can be added to the compositions before they are used. However, it is preferred not to use any organic solvents in the polyisocyanate composition of the present invention.

In one preferred embodiment, the water dispersible isocyanate  
5 component comprises BAYHYDUR XP7065 isocyanate, commercially available from Bayer Corporation.

The relatively high solids concentration of an water-based coating composition of this invention can be achieved either directly, for example so as to realize the high solids concentration upon solubilization or dispersion in aqueous  
10 medium, or can be achieved upon the stripping (e.g., under vacuum) of solvent and/or water from an aqueous solution or dispersion of the vinyl-type polymer.

An important characteristic of the water-based coating compositions made in accordance with this invention is that they are essentially colloidal silica-free. In other words, these coating compositions are essentially free of dispersed  
15  $\text{SiO}_2$  having particle sizes ranging from 4 to 100 nanometers. Generally, the water-based coating compositions of the invention will contain less than 10 parts by weight solids of such dispersed colloidal silica per 100 parts by weight solids of the vinyl-type polymer.

The stable, water-based, colloidal silica-free, coating composition of  
20 the present invention has a total organic resin solids content of greater than or equal to 25 percent by weight. At least 50 percent by weight of the total organic resin solids content consists of a solution-polymerized vinyl-type polymer (as described herein previously) having acid functionality sufficient to provide an acid value ranging from 5 to 160 and sufficient hydrolyzable silyl groups to provide a silicone  
25 content ranging from 0.40 to 6.0 percent by weight, preferably from 0.50 to 3.0 percent by weight. These weight percentages are based upon the total weight of the vinyl-type polymer. present in the water-based coating composition.

In addition to the foregoing components, the non-foaming, water-based coating compositions made in accordance with this invention may also include

optional ingredients generally known for use in coating compositions: Examples of such optional components include: fillers, defoamers, plasticizers, antioxidants, mildewcides and fungicides, surfactants, flow control agents and additives for sag resistance and/or pigment orientation based on polymer microparticles (sometimes referred to as microgels), and other such formulating additives. Additionally, where desired compositions of the invention may contain various solvents and pigments.

Water-based coating compositions of the invention may be applied over a wide variety of substrates such as wood, metals, glass, cloth, plastics, foams and the like, as well as over primers. They can be applied by any known method, including: brushing, dipping, flow coating, roll coating, curtain coating *etc.*

## EXAMPLES

The following examples illustrate the invention and should not be construed at a limitation on the scope thereof. Unless specifically indicated otherwise, all percentages and amounts are understood to be by weight.

Examples 1 through 3 illustrate the preparation of solution polymerized, acid-functional, vinyl-type polymers.

Examples 4 through 10 illustrate the preparation of coatings using, among other things, polymers made in Examples 1 through 3.

### EXAMPLE 1

This Example illustrates the preparation of a vinyl-type polymer product having hydrolyzable silyl groups incorporated onto its backbone which can be used as the water-based, hydroxy functional, acrylic polymeric component of the present invention.

### Stage I

To a reactor equipped with a stirrer and a nitrogen atmosphere 17.9 kg of 1-methoxy-2-propanol (solvent) were charged. While the solvent was refluxing, the following components were also charged into the reactor over 210 minutes: 10.9 kg 1-methyl-2-pyrrolidinone, and 2.3 kg VAZO 67<sup>®</sup> azo initiator (available from du Pont). Then, 5 minutes after the initiator feed, the reactor was also charged with the following over 180 minutes: 24.5 kg methyl methacrylate, 20.4 kg butyl acrylate, 3.6 kg acrylic acid, and 8.7 kg trimethoxymethacrylate-propyl silane.

The reaction was permitted to reflux throughout the additions set out above. Thereafter, 2.45 kg of 1-methoxy-2-propanol was used for tank rinses, rinsing into the reactor. After the feeds were completed, the resin was held at reflux for 2 hours.

### Stage II

After reflux was completed, the reactor contents were cooled to 28° C. The following components were then charged sequentially to the reactor with stirring: 37.1 kg methyl methacrylate, 22.6 kg hydroxyethyl methacrylate, 50.9 kg butyl acrylate, and 4.6 kg N,N-dimethylaminoethanol. Then, after stirring for 10 minutes, the reactor's contents were poured, over a 20 minute period, into a vessel. The vessel into which the reactor's contents were poured contained the following components: 252.6 kg deionized water, which was nitrogen purged, 3.7 g ferrous ammonium sulfate, and 2.5 kg deionized water (used to dissolve the ferrous ammonium sulfate). Then, the following solution was to the vessel added over 5 minutes: 6.8 kg deionized water, and 0.3 kg isoascorbic acid.

The temperature of the liquid in the vessel was then adjusted to a temperature of 29° C. Following this temperature adjustment, the following solution was added to the vessel over 15 minutes: 0.4 kg 35% hydrogen peroxide,



and 20.5 kg deionized water. Thereafter, 2.3 kg deionized water was then added as a tank rinse.

The polymerization proceeded exothermically. After stirring for 1 hour after the exotherm has peaked, the material is discharged from the vessel.

- 5           The resulting vinyl-type polymer product's solids concentration as measured at 110° C. for 1 hour was 34.75 percent; the product's viscosity was 15 cps; and the product's density was 1.0 g/cc.

## EXAMPLE 2

- 10           This Example illustrates the preparation of a vinyl-type polymer product which does not have hydrolyzable silyl groups incorporated onto its backbone.

- Using essentially the same procedure set out in Example 1, a vinyl-type polymer was prepared. The only significant differences were the components  
15   used in Stages I and II.

          The components used in Stage I of this Example were as follows:  
311.9 g 1-methoxy-2-propanol, 189.9 g 1-methyl-2-pyrrolidinone, 40.5 g VAZO 67® azo initiator, 498.8 g methyl methacrylate, 415.2 g butyl acrylate, 100.5 g acrylic acid, and 61.8 g 1-methoxy-2-propanol rinse.

- 20           The components used in Stage II of this Example were as follows:  
314.4 g of product from Stage I of this Example, 134.9 g methyl methacrylate, 77.1 g hydroxyethyl methacrylate, 173.5 g butyl acrylate, 19.9 g N,N-dimethylaminoethanol, 883.9 g deionized water, 1.3 g 1% ferrous ammonium sulfate solution, 0.89 g isoascorbic acid, 15.0 g deionized water, 0.9 g 50%  
25   hydrogen peroxide, and 72.8 g deionized water.

          The resulting vinyl-type polymer product's solids concentration was 34.8 percent; the product's viscosity was 15 cps; and the product's density was 1.0 g/cc.

### EXAMPLE 3

This Example illustrates the preparation of a vinyl-type polymer product which does not have hydrolyzable silyl groups incorporated onto its backbone.

Using essentially the same procedure set out in Example 1, a vinyl-type polymer was prepared. The only significant differences were the components used in Stages I and II.

The components used in Stage I of this Example were as follows:

311.9 g 1-methoxy-2-propanol, 189.9 g 1-methyl-2-pyrrolidinone, 40.5 g VAZO 67<sup>®</sup> azo initiator, 424.5 g methyl methacrylate, 429 g butyl acrylate, 85.5 g acrylic acid, 75.6 g styrene, and 42.6 g 1-methoxy-2-propanol rinse.

The components used in Stage II of this Example were as follows:

314.4 g of product from Stage I of this Example, 134.9 g methyl methacrylate, 77.1 g hydroxyethyl methacrylate, 173.5 g butyl acrylate, 15.9 g N,N-dimethylaminoethanol, 883.9 g deionized water, 1.3 g 1% ferrous ammonium sulfate solution, 0.9 g isoascorbic acid, 15.0 g deionized water, 0.9 g 50% hydrogen peroxide, and 72.8 g deionized water.

The resulting vinyl-type polymer product's solids concentration was 34.8 percent; the product's viscosity was 17 cps; and the product's density was 1.0 g/cc.

## EXAMPLE 4

This Examples illustrates the preparation of a water-based coating composition by blending, under mild agitation, the following components:

92.5g	Vinyl-type polymer (EXAMPLE 1)
0.4 g	DREWPLUS L-405 <sup>a</sup>
0.7 g	TINUVIN 292 <sup>b</sup>
0.7 g	TINUVIN 1130 <sup>c</sup>
3.8 g	DOWANOL PM <sup>d</sup>
0.9 g	ZONYL FSN <sup>e</sup>
1.0 g	Intermediate

5

<sup>a</sup> Commercially available from Drew Industrial.

<sup>b</sup> Commercially available from Ciba Additives.

<sup>c</sup> Commercially available from Ciba Additives.

<sup>d</sup> Commercially available from Dow Chemical.

10

<sup>e</sup> Commercially available from DuPont.

Thereafter, 14.4 g of BAYHYDUR XP7065 isocyanate was slowly added to blend and stirred under mild agitation for approximately 2 minutes. This mixture was then filtered through a fine mesh paper filter.

15

Next, 100 ml of the filtered mixture was weighed into a graduated beaker. The weight of the 100 ml sample was recorded as the initial weight. This mixture is hereinafter referred to as "Coating 1."

Coating 1 was observed over the next 24 hours, at which time it was re-weighed and any volume change due to the formation of foam was recorded in TABLE 1 *infra*. The rating scheme used to quantify the amount of foam generated was as follows:

20

Rating Number	Final Volume after 24 Hours (millimeters)
1	100-105
2	106-115
3	116-130
4	131-145
5	> 146

### EXAMPLE 5

This Examples illustrates the preparation and testing of a water-based coating composition in a manner analogous to that described in Example 4. The  
5 coating prepared in this Example is hereinafter referred to as "Coating 2."

The only significant difference between Coating 1 and Coating 2 is that, in the preparation of Coating 2, the DREWPLUS L 405 defoamer was not used.

10

### EXAMPLE 6

This Examples illustrates the preparation and testing of a water-based coating composition in a manner analogous to that described in Example 4. The coating prepared in this Example is hereinafter referred to as "Coating 3."

15 The only significant difference between Coating 1 and Coating 3 is that, in the preparation of Coating 3, the 92.5g vinyl-type polymer from EXAMPLE 1 was replaced with 92.5g E3275 acrylic polyol commercially available from Rohm and Haas; and 13.2 g of BAYHYDUR XP7065 isocyanate was used.

### EXAMPLE 7

This Examples illustrates the preparation and testing of a water-based coating composition in a manner analogous to that described in Example 4. The coating prepared in this Example is hereinafter referred to as "Coating 4."

5           The only significant difference between Coating 1 and Coating 4 is that, in the preparation of Coating 4, all that was blended together was 86.5 g vinyl-type polymer from EXAMPLE 1 and 13.5g of BAYHYDUR XP7065 isocyanate.

### EXAMPLE 8

10           This Examples illustrates the preparation and testing of a water-based coating composition in a manner analogous to that described in Example 4. The coating prepared in this Example is hereinafter referred to as "Coating 5."

          The only significant difference between Coating 1 and Coating 4 is that, in the preparation of Coating 5, all that was blended together was 86.5 g vinyl-type polymer from EXAMPLE 2 and 13.5g of BAYHYDUR XP7065 isocyanate.

15

### EXAMPLE 9

          This Examples illustrates the preparation and testing of a water-based coating composition in a manner analogous to that described in Example 4. The coating prepared in this Example is hereinafter referred to as "Coating 6."

20

          The only significant difference between Coating 1 and Coating 4 is that, in the preparation of Coating 6, all that was blended together was 86.5 g vinyl-type polymer from EXAMPLE 3 and 13.5g of BAYHYDUR XP7065 isocyanate.

## EXAMPLE 10

This Examples illustrates the preparation and testing of a water-based coating composition in a manner analogous to that described in Example 4. The coating prepared in this Example is hereinafter referred to as "Coating 7."

5 The only significant difference between Coating 1 and Coating 7 is that, in the preparation of Coating 7, all that was blended together was 86.50 g vinyl-type polymer from EXAMPLE 1 and 13.5g of TOLONATE XWHDT-102 isocyanate commercially available from Rhodia, Inc.

10

## TEST RESULTS

The weight and volume change data collected from testing Coatings 1-7 is set out in TABLE 1.

TABLE 1

Coating Number	Foaming Rating (After 24 Hours)
1	1
2	1
3	4
4	1
5	3
6	5
7	2

15

As stated earlier, an foaming rating of 1 represented a volume change due to foam generation of less than 5 percent. With this in mind, it was surprising to observe that coatings made in accordance with the present invention (*i.e.*, Coatings 1, 2 and 4) all were essentially foam free after 24 hours in storage. On the other hand, a coating made with the same resin but a different crosslinker (*i.e.*,

20

Coating 7); and those made with the different resins but the same crosslinker (*i.e.*, Coatings 3, 5 and 6); all generated foam which makes them cumbersome to use, even if at all possible, in a commercial setting.

- 5           It is evident from the foregoing that various modifications, which are apparent to those skilled in the art, can be made to the embodiments of this invention without departing from the spirit or scope thereof. Having thus described the invention, it is claimed as follows.

**WHAT IS CLAIMED IS:**

1. A non-foaming, water-based coating composition comprising the reaction product of:

- 5                   a) a water-based, hydroxy functional, acrylic polymeric component comprising a vinyl-type polymer product having hydrolyzable silyl groups incorporated onto its backbone, and
- b) a water dispersible isocyanate component comprising a polyisocyanate composition based on hexamethylene diisocyanate

10

2. The non-foaming, water-based coating composition of claim 1 wherein the vinyl-type polymer has:

- a) acid functionality sufficient to provide an acid value of from 5 to 160 and a hydroxyl value of less than or equal to 10 and
- 15                  b) sufficient hydrolyzable silyl groups to provide a Si content in the range of from 0.40 to 6.0 percent by weight based on the total weight of said vinyl-type polymer.

3. The non-foaming, water-based coating composition of claim 2

20 wherein the Si atoms of said vinyl-type polymer's hydrolyzable silyl groups are separated by at least two atoms from the backbone of said vinyl-type polymer.

4. The non-foaming, water-based coating composition of claim 1 wherein the vinyl-type polymer is prepared from the copolymerization of

25 components comprising an ethylenically unsaturated silane monomer containing at least one hydrolyzable silyl group, an ethylenically unsaturated acid and/or anhydride thereof, and at least one other copolymerizable vinyl-type monomer.



5. The non-foaming, water-based coating composition of claim 1 wherein the vinyl-type polymer is prepared from the copolymerization of components comprising an ethylenically unsaturated anhydride and at least one other  
5 copolymerizable vinyl-type monomer wherein amino functionality of an amino-functional compound containing at least one hydrolyzable silyl group has been reacted with an anhydride group of said vinyl-type polymer.

6. The non-foaming, water-based coating composition of claim 1  
10 wherein the vinyl-type polymer, prior to dispersion in water, has a number average molecular weight of not greater than 12,000, as determined by gel permeation chromatography utilizing a polystyrene standard.

7. The non-foaming, water-based coating composition of claim 4  
15 wherein the vinyl-type polymer is prepared from components comprising:

a) from 5 to 13 percent by weight of said ethylenically unsaturated acid and/or acid anhydride thereof,

b) from 12 to 87 percent by weight of said other copolymerizable vinyl-type monomer, and

20 c) an amount of said ethylenically unsaturated silane monomer to provide said Si content,

said percentages being based on the total weight of copolymerizable monomers used in the preparation of said vinyl-type polymer.

25 8. The non-foaming, water-based coating composition of claim 4 wherein said unsaturated acid and/or acid anhydride comprises a carboxylic acid and/or acid anhydride.

9. The non-foaming, water-based coating composition of claim 1 wherein the polyisocyanate composition based on hexamethylene diisocyanate has an average NCO functionality of 2 to 6 and comprises:

5                   a) a polyisocyanate adduct prepared from 1,6-hexamethylene diisocyanate or a mixture of hexamethylene diisocyanate with up to 70% by weight, based on the weight of the diisocyanates, of another diisocyanate, and

10                   b) an emulsifier present in an amount sufficient to provide an ethylene oxide content of at least 10% by weight based on the weight of the polyisocyanate composition, said emulsifier comprising the reaction product of:

15                   i) a monohydroxy functional polyether wherein the ethylene oxide portion of the polyether has a molecular weight of 200 to 1000 and the polyether has a total molecular weight of 200 to 1500 with

20                   ii) either the polyisocyanate adduct prepared from 1,6-hexamethylene diisocyanate or a mixture of hexamethylene diisocyanate with up to 70% by weight, or another polyisocyanate.

# INTERNATIONAL SEARCH REPORT

Internati- Application No  
PCT/US 99/09729

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G18/62 C09D175/04 C08G18/70

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 665 252 A (KANSAI PAINT CO LTD) 2 August 1995 (1995-08-02) page 2, line 1 - page 9, line 30 example 1	1,9
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A	DE 196 13 629 A (KANSAI PAINT CO LTD) 10 October 1996 (1996-10-10) page 2, line 28 - page 3, line 56 example 8	1-4,7,8
A	EP 0 571 187 A (NIPPON PAINT CO LTD) 24 November 1993 (1993-11-24) example 1; table 1	1,6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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